



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification<sup>5</sup> :</b> <b>C09J 7/02, 133/08</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 92/11332</b> <b>(43) International Publication Date:</b> <b>9 July 1992 (09.07.92)</b>
<b>(21) International Application Number:</b> PCT/US91/07779 <b>(22) International Filing Date:</b> 21 October 1991 (21.10.91) <b>(30) Priority data:</b> 632,116 20 December 1990 (20.12.90) US <b>(71) Applicant:</b> MINNESOTA MINING AND MANUFACTURING COMPANY [US/US]; 3M Center, P.O. Box 33427, Saint Paul, MN 55133-3427 (US). <b>(72) Inventors:</b> KRECKEL, Karl, W. ; Benzenbergweg 3, D-5657 Haan (DE). KARIM, Naimul ; Biberstrasse, D-4044 Kaarst 1 (DE). <b>(74) Agents:</b> JOSEPHS, Barry, D. et al.; Intellectual Property Counsel, Minnesota Mining and Manufacturing Company, Post Office Box 33427, St Paul, MN 55133-3427 (US).		<b>(81) Designated States:</b> AT (European patent), AU, BE (European patent), BR, CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, KP, LU (European patent), NL (European patent), SE (European patent).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> REMOVABLE ADHESIVE TAPE  <b>(57) Abstract</b>  A removable pressure-sensitive adhesive tape comprising a highly extensible backing, bearing on at least one major surface thereof a layer of photopolymerized acrylic pressure-sensitive adhesive, said tape being capable of being firmly bonded to a substrate and being further capable of being removed therefrom after only being stretched at an angle no greater than about 35° from the surface of the substrate.		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	ES	Spain	MG	Madagascar
AU	Australia	FI	Finland	ML	Mali
BB	Barbados	FR	France	MN	Mongolia
BE	Belgium	GA	Gabon	MR	Mauritania
BF	Burkina Faso	GB	United Kingdom	MW	Malawi
BG	Bulgaria	GN	Guinea	NL	Netherlands
BJ	Benin	GR	Greece	NO	Norway
BR	Brazil	HU	Hungary	PL	Poland
CA	Canada	IT	Italy	RO	Romania
CF	Central African Republic	JP	Japan	SD	Sudan
CG	Congo	KP	Democratic People's Republic of Korea	SE	Sweden
CH	Switzerland			SN	Senegal
CI	Côte d'Ivoire	KR	Republic of Korea	SU <sup>+</sup>	Soviet Union
CM	Cameroon	LI	Liechtenstein	TD	Chad
CS	Czechoslovakia	LK	Sri Lanka	TG	Togo
DE*	Germany	LU	Luxembourg	US	United States of America
DK	Denmark	MC	Monaco		

+ Any designation of "SU" has effect in the Russian Federation. It is not yet known whether any such designation has effect in other States of the former Soviet Union.

REMOVABLE ADHESIVE TAPEBackground of the Invention

5

Field of the Invention

The invention relates to a high performance pressure-sensitive adhesive tape comprising a backing and an acrylic pressure-sensitive adhesive layer, that can be firmly adhered to a substrate and yet be removed without damage to the substrate, and substantially without adhesive transfer to the substrate.

Description of the Related Art

Acrylic pressure-sensitive adhesive tapes are well known in the art. They are primarily used in applications requiring high adhesion and shear properties, such as the automotive industry. Once placed, these tapes are not ordinarily removable. Delicate substrates would suffer substantial damage; substrates such as stainless steel would not suffer damage; however, because such tapes typically have an adhesive strength which is greater than the cohesive strength, the tape would not cleanly remove, but would leave large portions of adhesive, both with and without backing, on the substrate. In the case of a double-coated pressure-sensitive adhesive tape, removability would be even more difficult, as no large surface of the tape would be available to grasp or peel. Attempting removal of such a tape would typically require destruction or grave damage to at least one of the substrates. Even metal substrates would be deformed in an attempt to peel the two substrates apart.

Acrylic copolymer adhesives are well known in the art as high performance permanent bond adhesives. In U.S. Patent No. 24, 906, (Ulrich), alkyl acrylate copolymers are described which are predominantly alkyl esters of acrylic acid having from 4 to 14 carbon atoms, and further comprise a minor amount (3-12%, preferably 4-

-2-

8%) of a polar copolymerizable monomer such as acrylic acid. Such adhesives are widely popular as they are readily available and provide a good balance of tack, shear and peel properties on a variety of substrates at a relatively low cost.

U.S. Patent No. 4,181,752, (Martens et al.) discloses a process of ultraviolet photopolymerization of alkyl acrylate esters and polar copolymerizable monomers to form the acrylate copolymer. Martens teaches that intensity and spectral distribution of the irradiation must be controlled in order to attain desirable cohesive strengths and peel resistance. The photopolymerization is preferably carried out in an inert atmosphere as oxygen tends to inhibit the reaction. Adhesive properties for tapes made via the Martens process are improved over those made by solution polymerization. Further, because of the vast reduction in solvents required, the tapes are produced in a more environmentally responsible manner. Numerous references disclose pressure-sensitive adhesives comprising photopolymerized acrylic copolymers, including U.S. Patent Nos. 4,223,067, and 4,415,615, which disclose conformable foam or foamlike pressure-sensitive adhesives.

Various types of removable adhesives are also well known in the art. Some are permanently removable, and are also called "repositionable". Particulate adhesives are known to be useful in removable pressure-sensitive adhesive applications. Microsphere-based adhesives perform particularly well in such applications. Numerous references concern the preparation and/or use of inherently tacky, elastomeric acrylate microspheres. Such spheres are disclosed in U.S. Patent No. 3,691,140, (Silver). These microspheres are prepared by aqueous suspension polymerization of alkyl acrylate monomers and ionic comonomers, e.g., sodium methacrylate, in the

-3-

presence of an anionic emulsifier. The use of a water-soluble, substantially oil-insoluble ionic comonomer is critical to preventing coagulation or agglomeration of the microspheres.

5 U.S. Patent No. 4,166,152, (Baker et al.) discloses solid, inherently tacky (meth)acrylate microspheres which are prepared from non-ionic alkyl acrylate or methacrylate monomers in the presence of both an emulsifier and an ionic suspension stabilizer having  
10 an interfacial tension sufficient to prevent microsphere agglomeration.

U.S. Patent No. 4,968,562 (Delgado) discloses hollow, inherently tacky, acid-free acrylic microspheres having multiple inclusions, each inclusion being less  
15 than 10% of the diameter of the microsphere, the total inclusions being more than 10% of the diameter of the microsphere.

One problem with microsphere adhesives or other repositionable adhesives is that they are permanently  
20 removable and repositionable. They are not capable of permanent adhesion should such become desirable.

U.S. Patent No. 4,024,312 (Korpman) discloses an easily removable pressure-sensitive adhesive tape which may be removed by stitching it length-wise in a  
25 direction substantially parallel to the surface. The backing is disclosed to possess an elastic recovery from 50% of at least 75%. Useful adhesives may be conventional rubber resin adhesives or ABA block copolymers, in which case a tackifier must also be  
30 included. No high performance adhesives or acrylic adhesives are disclosed.

Another type of removable pressure-sensitive adhesives is a temporarily removable adhesive. One commercially available type of adhesive contains hollow  
35 spheroidal particles, as described in U.S. Patent Nos. 3,314,834, and 3,331,729, adhesive-coated particle is

-4-

placed into position and may be adjust until a satisfactory position is reached. When permanent adhesion is desired, sufficient pressure must be applied, either by hand or roller, to rupture the hollow particles. A permanent bond is then established.

Other references disclose various pressure-sensitive adhesives which do not develop permanent adhesion for a period of time in order to allow some degree of removability. See e.g., U.S. Patent Nos. 3,770,708, 3,857,731, and 3,922,464.

However, none of the adhesives disclosed above have high adhesive performance, i.e., high shear and tack such that the adhesive may remain permanently bonded to the substrate, if desired, and yet possess a mechanism for long term removability without damage to the substrate or adhesive transfer.

#### Summary of the Invention

The present invention provides a removable pressure-sensitive adhesive tape comprising a highly extensible backing, bearing on at least one major surface thereof a layer of photopolymerized acrylic pressure-sensitive adhesive, said tape being capable of being firmly bonded to a substrate and being further capable of being removed therefrom after only being stretched at an angle no greater than about 35° from the surface of the substrate.

In preferred removable pressure-sensitive adhesive tapes of the invention, the acrylic pressure-sensitive adhesive comprises an acrylic polymer of monomers containing:

- a) at least about 70 parts of an alkyl acrylate monomer, the alkyl groups of which have an average of 4 to 12 carbon atoms, and
- b) from 0 to about 30 parts of a monoethylenically unsaturated monomer, and

-5-

c) from about 0.01 part to about 1 part of a photoinitiator.

The tape can be firmly bonded to a substrate and then can be removed by simply stretching the tape in a direction up to an angle of about 35° from the surface of the substrate, preferably up to about 30°, more preferably up to about 10° without leaving traces of adhesive residue, and without imparting any perceptible damage to the surface of the substrate.

The invention further provides a double-coated tape comprising a backing bearing adhesive layers on both major surfaces thereof. The adhesive of each layer can be similar or different chemical composition, of equivalent of different adhesion properties, of equivalent or different thickness, and coated or laminated in the same or different manner. Preferred double-coated tapes comprise high-performance acrylic adhesive layers on both major surfaces.

#### Detailed Description of the Invention

Acrylic pressure-sensitive adhesives useful in tapes of the invention are formed from at least one alkyl acrylate monomer, preferably a monofunctional unsaturated acrylate ester or non-tertiary alkyl alcohol, the alkyl groups of which have from 1 to about 14 carbon atoms. Included within this class of monomers are, for example, isooctyl acrylate, isononyl acrylate, 2-ethylhexyl acrylate, decyl acrylate, dodecyl acrylate n-butyl acrylate, and hexyl acrylate. The alkyl acrylate monomers can be used to form homopolymers, or they can be copolymerized with polar copolymerizable monomers or modifying monomers.

Useful polar copolymerizable monomers are selected from strongly polar and moderately polar monomers. When strongly polar monomers are used, the alkyl acrylate monomer generally comprises at least about

-6-

75% of the final polymer, preferably from about 85% to about 95%. When copolymerized with moderately polar copolymerizable monomers, the alkyl acrylate monomer generally comprises at least about 70% if the  
 5 photopolymerized final polymer, preferably from about 70% to about 95%.

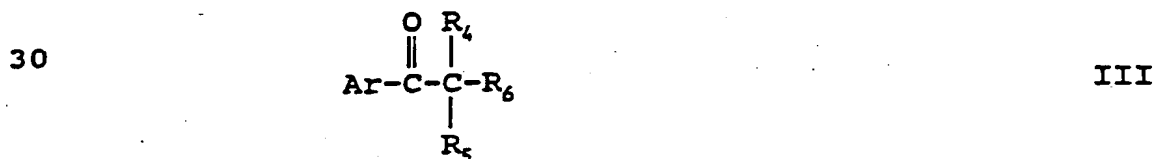
Strongly polar monomers include acrylic acid, itaconic acid, hydroxyalkyl acrylates, cyanoalkyl acrylates, acrylamides, and substituted acrylamides.

10 Useful moderately polar monomers include N-vinyl caprolactam, N-vinyl pyrrolidone, acrylonitrile, vinyl chloride and diallyl phthalate.

The pressure-sensitive adhesive compositions also contain a free-radical photoinitiator to induce  
 15 photopolymerization.

The free-radical photoinitiator can be selected from those compounds disclosed in "Mechanisms of the Photodecomposition of Initiators", George F. Vesley, Journal of Radiation Curing<sup>™</sup>, January, 1986, incorporated  
 20 herein by reference. They are selected from acetophenones and ketals, benzophenones, aryl glyoxalates, acylphosphine oxides, sulfonium and iodonium salts, diazonium salts and peroxides. Preferred additional free-radical photoinitiators are those that  
 25 have an absorption maximum in the 300 to 400 nm region of the electromagnetic spectrum.

Especially useful are acetophenones and ketals corresponding to the formula:



35 wherein Ar is C<sub>6</sub>-C<sub>14</sub> aryl which is unsubstituted or substituted by halogen, CN, OH, C<sub>1</sub>-C<sub>12</sub> alkyl, -alkoxy, -phenoxy, -thioalkyl, -SCH<sub>2</sub>CH<sub>2</sub>OH, -thiophenyl, -SO<sub>2</sub>alkyl, -SO<sub>2</sub>phenyl, -COOalkyl, -SO<sub>2</sub>NH<sub>2</sub>, -SO<sub>2</sub>N-Halkyl, -SO<sub>2</sub>N(alkyl)<sub>2</sub>,



-7-

-NHalkyl, -N(alkyl)<sub>2</sub>, -NHCOalkyl or -NHCO-phenyl, or represents thienyl, pyridyl, furyl, indanyl or tetrahydronaphthyl, and alkyl represents a lower alkyl radical of 1 to 4 carbon atoms; R<sub>4</sub> is OH, C<sub>1</sub>-C<sub>8</sub> alkyl which is unsubstituted or substituted by -OH, alkoxy, C<sub>2</sub>-C<sub>8</sub> acyloxy, -COOalkyl or CN, or is C<sub>3</sub>-C<sub>4</sub> alkylenyl, C<sub>5</sub>-C<sub>6</sub> cycloalkyl, C<sub>7</sub>-C<sub>8</sub> phenylalkyl, or -OR<sub>7</sub> wherein R<sub>7</sub> is C<sub>1</sub>-C<sub>8</sub> alkyl which is unsubstituted or substituted by -OH, alkoxy, C<sub>2</sub>-C<sub>8</sub> acyloxy, -COO alkyl, -CN or phenyl, or C<sub>6</sub> aryl; and R<sub>5</sub> has one of the meanings assigned to R<sub>3</sub>, C<sub>2</sub>-C<sub>8</sub> alkylene or together with R<sub>3</sub> represents C<sub>2</sub>-C<sub>8</sub> alkylene or C<sub>3</sub>-C<sub>9</sub> oxaalkylene or azaalkylene; and R<sub>6</sub> is hydrogen, OH, C<sub>1</sub>-C<sub>8</sub> alkyl, C<sub>6</sub>-C<sub>14</sub> aryl, C<sub>5</sub>-C<sub>8</sub> cycloalkyl or morpholino.

Such compounds have been disclosed, for example, in U.S. Patent No. 3,715,293, U.S. Patent No. 3,728,377, U.S. Patent No. 4,284,485 and U.S. Patent No. 4,318,791, all of which are incorporated herein by reference.

Preferred compounds have R<sub>4</sub> and R<sub>5</sub> as -OR<sub>7</sub>, R<sub>7</sub> as C<sub>1</sub>-C<sub>4</sub> alkyl and R<sub>6</sub> phenyl; or R<sub>4</sub> and R<sub>5</sub> combining to form C<sub>2</sub>-C<sub>8</sub> alkylene, preferably cyclohexylene, and R<sub>6</sub> as -OH or phenyl.

Typical alkyl groups include methyl, ethyl, propyl, isobutyl, t-butyl, pentyl, neopentyl, hexyl, heptyl, octyl, 2-ethylhexyl; aryl groups include phenyl, naphthyl, anthracyl, tolyl, xylyl, methoxyphenyl, halophenyl, hydroxyphenyl, nitrophenyl and carboethoxyphenyl; and cycloalkyl groups include cyclopentyl, methylcyclopentyl, dimethylcyclopentyl, ethylcyclopentyl, cyclohexyl, methylcyclohexyl, cycloheptyl, bicycloheptyl, cyclooctyl, and bicyclooctyl.

Illustrative thereof are

2,2-dimethoxyacetophenone,  
2,2-dimethoxy-2-phenylacetophenone,  
2-diethoxyacetophenone, 2,2-dibutoxyacetophenone,

-8-

2,2-dihexoxyacetophenone,  
2,2-di(2-ethylhexoxy)acetophenone,  
2,2-diphenoxyacetophenone, 2,2-ditolylloxyacetophenone,  
2,2-di(chlorophenyl)acetophenone,  
5 2,2-di(nitrophenyl)acetophenone,  
2,2-diphenoxy-2-phenylacetophenone,  
2,2-dimethoxy-2-methylacetophenone,  
2,2-dipropoxy-2-hexylacetophenone,  
2,2-diphenoxy-2-ethylacetophenone,  
10 2,2-dimethoxy-2-cyclopentylacetophenone,  
2,2-di(2-ethylhexyl)-2-cyclopentylacetophenone,  
2,2-diphenoxy-2-cyclopentyl-acetophenone,  
2,2-di(nitrophenoxy)-2-cyclohexylacetophenone,  
2,2-dimethyl-2-hydroxyacetophenone,  
15 2,2-diethoxy-2-phenylacetophenone,  
2,2-diphenethyloxy-2-phenylacetophenone,  
2,2-(2-butenediylloxy)-2-phenylacetophenone,  
2,2-dimethyl-2-morpholino-(p-thiomethyl)acetophenone, and  
1-hydroxycyclohexyl phenyl ketone.

20 Also preferred are aromatic onium salts. These salts are disclosed, for example in U.S. Patent Nos. 4,069,054, 4,231,951 and 4,250,203. Such salts are described by the formula

25

AX

IV

wherein A is an organic cation selected from those described in U.S. Patent Nos. 3,708,296, 3,729,313, 3,741,769, 3,794,576, 3,808,006, 4,026,705, 4,058,401,  
30 4,069,055, 4,101,513, 4,216,288, 4,394,403, and 4,623,676, all of which incorporated herein by reference. A is preferably selected from diazonium, iodonium, and sulfonium cations, more preferably diphenyliodonium, triphenylsulfonium and phenylthiophenyl diphenylsulfonium  
35 X is an anion where X is the same as defined for formulas I and II. Preferably, the anions are  $\text{CF}_3\text{SO}_3^-$ ,  $\text{BF}_4^-$ ,  $\text{PF}_6^-$ ,

-9-

$\text{SbF}_6^-$ ,  $\text{SbF}_5\text{OH}^-$ ,  $\text{AsF}_6^-$ , and  $\text{SbCl}_6^-$ .

Phot initiators which are useful for partially polymerizing alkyl acrylate monomer without crosslinking, to prepare the partially polymerized syrup, discussed  
5 infra, include the benzoin ethers (such as benzoin methyl ether or benzoin isopropyl ether), substituted benzoin ethers (such as anisoin methyl ether), substituted acetophenones (such as 2,2-diethoxyacetophenone and 2,2-dimethoxy-2-phenylacetophenone), substituted  
10 alpha-ketols (such as 2-methyl-2-hydroxypropionophenone), aromatic sulfonyl chlorides (such as 2-naphthalenesulfonyl chloride) and photoactive oximes. Photoinitiators may be used for syrup-making in amounts which, when dissolved, provide about 0.001 to 0.5 percent  
15 by weight of the alkyl acrylate monomer, preferably at least 0.01 percent.

Where superior cohesive strengths are desired, the composition should be crosslinked. Useful crosslinking agents include multiacrylates such as 1,6-  
20 hexanediol diacrylate, as well as those disclosed in U.S. Patent No. 4,379,201, (Heilmann et al.), incorporated herein by reference. Other suitable crosslinking agents include hydrogen abstracting carbonyls such as anthraquinone and benzophenone and their derivatives, as  
25 disclosed in U.S. 4,181,752, (Martens). When crosslinking agents are used, they typically comprise from about 0.01% to about 1% of the total monomer weight.

Where concurrent photoinitiation and crosslinking is desirable, the specific photoactive  
30 chromophore-substituted-halomethyl-s-triazines disclosed in U.S. Patent Nos. 4,391,687 (Vesley) and 4,330,590, (Vesley) and 4,329,384 (Vesley et al.), all of which are incorporated herein by reference, are preferred. The preferred level of triazine taught ranges from 0.01 to  
35 about 2 parts of the crosslinking agent per 100 parts acrylic copolymer.

-10-

Useful pressure-sensitive adhesives in compositions of the invention include those which only become tacky at elevated temperatures, e.g., acrylic copolymers having average carbon-to-carbon chains of less than 4 carbon atoms, or those comprising a polymer wherein methacrylic acid esters are substituted for all or portions of the acrylic acid esters.

Where foam-like adhesives are desirable, i.e., in those applications requiring adhesive to low energy substrates, or to substrates having irregular surfaces, the pressure-sensitive adhesive may comprise microbubbles. Useful microbubbles include glass microbubbles, as taught in U.S. Patent No. 4,223,067 (Levens), and polymeric microbubbles as taught in U.S. Patent Nos. 3,615,972, (Nakayama), 4,075,138 (Beck), and 4,855,170, (Darvell), all of which are incorporated herein by reference. Polymeric microbubbles are available from Kema Nord under the trade name Expancel™. In expanded form, the microbubbles have a specific density of approximately 0.02-0.36 g/cc. It is possible to include unexpanded microbubbles in the pressure-sensitive adhesive composition and subsequently heat to expand, but it is preferred to mix the expanded microbubbles in the adhesive in order to assure that all microbubbles are surrounded by at least a thin layer of adhesive.

The microbubbles may be clear or colored as disclosed in U.S. Patent No. 4,612,242, (Vesley et al.) 4,618,525, (Chamberlain et al.) 4,666,771, (Vesley et al.), and 4,950,530 (Vesley et al.).

When used, microbubbles should have an average diameter of from about 10 to about 200 micrometers, and comprise from about 5 to about 65 volume percent of the pressure-sensitive adhesive layer. When glass microbubbles are used, the thickness of the foam-like layer should exceed three times the average diameter of

-11-

the microbubbles, and twice the diameter of substantially  
ev ry micr bubble.

One very useful filler is hydrophobic silica as  
defined in U.S. Pat. Nos. 4,710,536, and 4,749,590,  
5 (Klingen et al.), both of which are incorporated herein  
by reference. In one preferred embodiment of the  
invention, one or more layers of the pressure-sensitive  
adhesive tape contain from about 2 to about 15 parts of a  
hydrophobic silica having a surface area of from 50 to  
10 about 400 m<sup>2</sup>/g.

Other useful filler materials include fibrous  
reinforcement strands, dyes, pigments, viscosity  
adjusting agents, chain transfer agents, and the like.

In one preferred embodiment of the pressure-  
15 sensitive adhesive tape of the invention, the pressure-  
sensitive adhesive comprises an acrylic cellular  
pressure-sensitive adhesive membrane layer (CPSAM). The  
cellular pressure-sensitive adhesive membrane has a  
cellular structure providing at least 10% voids, such  
20 percentage being on a volume basis. The average size of  
the voids is calculated as follows:

du= the unfoamed density of the adhesive  
membrane

df=the foamed density of the adhesive membrane  
25 v= voids in the adhesive membrane

$$v = \frac{du - df}{du}$$

It is preferable to include a surfactant in the  
30 composition of a CPSAM. Preferred surfactants are those  
such as fluorochemicals known to be useful for foaming  
organic materials with low surface tension. By doing so,  
tapes with membranes of good uniformity will be produced  
wherein the cells have an average diameter within the  
35 range of 0.05 to 0.3 mm. Typically, 90% of the cells of  
the adhesive membrane vary in size no more than 2:1.  
CPSAM adhesive layers may range from about 2.0 mm in

-12-

thickness to about 10 mm.

A cellular pressure-sensitive adhesive membrane is made by the steps of

- a) frothing a composition which is
- 5 polymerizable to a pressure-sensitive adhesive state,
- b) coating the froth onto a backing, and
- c) polymerizing the coated froth in situ to a pressure-sensitive adhesive state to provide a pressure-sensitive adhesive membranes having a cellular structure.

10 Frothing can be conveniently accomplished by whipping a gas into the polymerizable mixture.

The pressure-sensitive adhesive compositions useful in tapes of the invention are preferably prepared by premixing together the

15 photopolymerizable monomers and the photoinitiator. This premix is then partially polymerized to a viscosity in the range of from about 500 centipoise (cps) to about 50,000 cps to achieve a coatable syrup. Alternatively, the monomers can be mixed with a thixotropic agent such

20 as a hydrophilic fumed silica to achieve a coatable syrup composition.

The composition is then coated onto the backing, or onto a flexible carrier web and polymerized in an inert, i.e., oxygen free atmosphere, e.g., a

25 nitrogen atmosphere. A sufficiently inert atmosphere can be achieved by covering a layer of the photoactive coating with a plastic film which is substantially transparent to ultraviolet radiation, and irradiating through that film in air using fluorescent-type

30 ultraviolet lamps which generally give a total radiation dose of about 500 millijoules/cm<sup>2</sup>. The coating of the tapes may be accomplished using any conventional means such as roller coating, dip coating or extrusion coating.

Pressure-sensitive adhesive tapes of the

35 invention may contain more than one layer. Such multilayered tapes may have a thin layer of a differing

-13-

acrylic pressure-sensitive adhesive laminated to a thicker, e.g., foamlike core adhesive layer. Alternatively, the "core" or inner layer may be a photopolymerizable composition which is not pressure-sensitive.

Where multilayer tape constructions are desirable, a preferred method of construction is multilayer coating as described in U.S. Patent Nos. 4,818,610, and 4,895,738, (Zimmerman et al.) and U.S. Patent No. 4,894,259, (Kuller), all of which are incorporated herein by reference. In multilayer coating, a plurality of copolymerizable coatable compositions are prepared, each composition containing at least one photopolymerizable monomer, one of the coatable compositions being the acrylic pressure-sensitive adhesive layer. The compositions are then coated to provide a plurality of superimposed layers with contiguous layers defining an interface therebetween, with the pressure-sensitive adhesive layer being coated as an outer layer. Migration of photopolymerizable monomers through the interface between contiguous layers is permitted, and the superimposed layers are then simultaneously irradiated. This provides polymeric chains comprised of copolymers of photopolymerizable monomers originating from contiguous layers which extend through the interface therebetween. Resulting tapes cannot be delaminated.

Useful backings for the pressure-sensitive adhesive tapes of the invention are highly extensible backings. The backings may be recoverable or substantially nonrecoverable.

Representative examples of materials suitable for the backing of the tape of this invention include polyolefins, such as polyethylene, including high density polyethylen, low density polyethylene, linear low density polyethylen, linear ultra low density

-14-

polyethylene, polypropylene, and polybutylenes; vinyl copolymers, such as polyvinyl chlorides, both plasticized and unplasticized, and polyvinyl acetates; olefinic copolymers, such as ethylene/methacrylate copolymers, 5 ethylene/vinyl acetate copolymers, acrylonitrile-butadiene-styrene copolymers, and copolymers; acrylic polymers and copolymers; and combinations thereof. Mixtures of blends of any plastic or plastic and elastomeric materials such as polypropylene/polyethylene, 10 polyurethane/polyolefin, polyurethane/polycarbonate, polyurethane/polyester can also be used.

Backings can be in the form of single or multilayer films, nonwoven films, porous films, foam-like films, and combinations thereof. Backings can also be 15 prepared from filled materials, such as, e.g., calcium carbonate filled polyolefins.

Where recoverable backings are desirable, above 75% recovery is preferred. Preferred recoverable materials include styrene containing A-B-A block 20 copolymers and blends of vinyl acetate and elastomers, with the most preferred material being a blend of ethylene copolymers and olefinic elastomers, available from Consolidated Thermoplastics Co. as "XQ 1099" and XQ 1901". Where nonrecoverable backings are desirable, 25 preferred materials are polyethylene and polypropylene, with low density and ultra low density polyethylenes being most preferred. Additional useful backings are thermoplastic blends of polypropylene and EPDM styrene copolymers and copolymers, available from CT 30 thermoplastics as XEL 12, XEL 36 and XEL 40, respectively.

Backings can be made by any known method of film forming, such as, extrusion, coextrusion, solvent casting, foaming, nonwoven technology, and the like. The 35 backing can be any thickness so long as it poss ss sufficient integrity to be processable and handleable,



-15-

with thickness  $s$  preferably ranging from about  $10\ \mu$  to about  $250\ \mu$ . Backings having thicknesses higher than about  $250\ \mu$  tend to require high than desired stretching force for removal.

5

### Test Methods

#### 90° Peel Adhesion

The adhesive layer to be tested is transferred to  $0.05\ \text{mm}$  thick, chemically primed, biaxially oriented poly(ethylene terephthalate) film which then is slit to a width of  $1.27\ \text{cm}$ . The resulting tape is self-adhered to a smooth stainless steel plate under the weight of a  $2.04\ \text{kg}$  hard-rubber-covered steel roller, two passes in each direction. After exposure to the indicated conditions, the peel adhesion is measured by moving the free end of the tape away from the steel plate at  $90^\circ$  at a rate of  $0.5\ \text{cm}$  per second using an Instron™ tensile tester.

15

#### Static Shear

This test employs two  $25.4\ \text{mm}$  wide stainless steel straps as follows: Type 304-2BA,  $0.38\ \text{mm}$  in thickness, surface roughness of  $0.05\ \text{micrometer}$  arithmetic average deviation from the main line. The strips are washed first with heptane, and a second wash with methyl ethyl ketone if heavy oils are present. A strip of  $25.4\ \text{mm}$  wide double-coated pressure-sensitive adhesive tape, carried on a low-adhesion liner, is adhered to one end of one of the straps and trimmed to a length of  $25.4\ \text{mm}$ . The liner is then removed, and the second strap is adhered to the exposed adhesive surface. The test assembly is placed in a horizontal position and  $1\ \text{kg}$  weight rests on the assembly for 15 minutes at room temperature to ensure bond between the surfaces. After dwelling at room temperature for 24 hours, the assembly is hung from one strap in an air-circulating oven which has been preheated to the indicated temperature

20

25

30

35

-16-

(typically 70°), and after 15 minutes, a weight is hung from the free end of the tape, with the top strap vertical. The time at which the weight falls is the "Static Shear Value". If no failure occurs, the test is discontinued at 10,000 minutes. Only cohesive failures are reported.

### Examples

#### Examples 1-12C

10       The following double-coated pressure-sensitive adhesive tapes were made to a thickness of 0.8 mm. The adhesive on both sides of each tape is identical.

Coatable syrups were first made for each pressure-sensitive adhesive layer.

15       The constructions were obtained by first coating the syrup onto the bottom liner, introducing the elastic backing, in tapes of the invention, and subsequently coating the second layer of syrup between the backing and the top liner.

20       Tapes 1-2 and 3C had an acrylic pressure-sensitive adhesive layer with a 90/10 ratio of isooctyl acrylate (IOA)/ acrylic acid (AA) having 0.2 part photoinitiator and 0.12 part 1,6-hexanediol diacrylate (HDDA). Tapes 1 and 2 were coated onto differing elastic  
25 film backings, "XQ 1900" and "XQ 1901" respectively, available from CT Plastics, Chippewa Falls, Wi. Tape 3C had no elastic backing.

      Tapes 4-5 and 6C had an acrylic pressure-sensitive adhesive layer with a 91/9 IOA/AA ratio having  
30 8 pph hollow glass bubbles, available from Minnesota Mining and Manufacturing Company (3M), 4 parts hydrophobic fumed silica, available as Aerosil™ R972, 0.13 part HDDA and 0.1 part Irgacure™ 651, a photoinitiator available from Ciba-Geigy. Tapes 4 and 5  
35 were coated onto differing elastic film backings, "XQ 1900" and "XQ 1901" respectively, available from CT

-17-

Plastics, Chippewa Falls, Wi. Tape 6C had no elastic backing. Backing A was 150  $\mu$  in thickness, and an elongation at break of 853%. Backing B was also 150  $\mu$  in thickness.

5                   Tapes 7-8 and 9C had an acrylic pressure-sensitive adhesive layer with a 91/9 IOA/AA ratio syrup with 2.2 pph polymeric microspheres, available as Expancel™ 551 De, 4 parts Aerosil™ R972, and 0.18 part Irgacure™ 651. Tapes 7 and 8 were coated onto differing  
10 elastic film backings, "XQ 1900" and "XQ 1901" respectively, available from CT Plastics, Chippewa Falls, Wi. Tape 9C had no elastic backing.

                  Tapes 10-11 and 12C had an acrylic pressure-sensitive adhesive layer with a 91/9 IOA/AA ratio syrup  
15 with 2.2 pph polymeric microspheres, available as Expancel™ 551 De, 4 parts Aerosil™ R972, and 0.18 part Irgacure™ 651. This tape was prepared by making a syrup as described above. The resulting mixture was mixed, and degassed. The mixture was then pumped into a 90 mm  
20 frother operating at 300-350 rpm. Concurrently, a 60/40 ratio of surfactants B and C as described in U.S. 4,415,615, (Esmay et al.) and nitrogen were fed into the frother. As the frother was continually fed with  
25 nitrogen, the mixture was delivered under 204 kPa pressure to the nip of a roll coater between a pair of sheets of transparent, biaxially-oriented poly(ethylene terephthalate), the faces of which had low adhesion coatings.

                  The composite emerging from the roll coater was  
30 irradiated with a bank of fluorescent black light bulbs, 90% of the emissions of which were between 300 and 400 nm, with a maximum at 351 nm with a total irradiation of 500 MJ, as measured by a Dynachem Radiometer™. Tapes 10 and 11 had XQ 1900" and "XQ 1901" respectively, film  
35 backings available from CT Plastics, Chippewa Falls, Wi., introduced as described above. Tape 12C used no elastic

-18-

backing.

The tapes were tested for 90° Peel adhesion to stainless steel and to paper, and the elastic backings were tested for mechanical properties. The test results are shown in Tables 1 and 2.

<u>Table 1</u>		
Example Number	Acrylic Copolymer Ratio	Backing Material
1	90/10	A
2	90/10	B
3C	90/10	none
4	91/9	QX 1900
5	91/9	QX 1901
6C	91/9	none
7	91/9	QX 1900
8	91/9	QX 1901
9C	91/9	none
10	91/9	QX 1900
11	91/9	QX 1901
12C	91/9	none

TABLE 2: PSA and Stretch Release Performance

Sample	90-Peel Adhesion to SS (N/0.5" to Paper (N/0.5") 20min.RT 3d,RT		Stretch Release (N/1") from Paper 20min.RT		Tensile Strength N/mm <sup>2</sup>	Elong. at break (%)	90-Peel Adhesion loss at 100% elong (N/dm) 20min.RT
	(N/dm)	(N/dm)	(N/dm)	(N/dm)			
1	470.9	248.8	PD (27.5)	78.3	112.2 <sup>a)</sup>	-	184.2
2	168.5	260.6	PD (26.0)	68.5	98.8 <sup>a)</sup>	-	184.2
3C	211.0	292.1	PD (29.1)	29.1	(2.0) <sup>b)</sup>	-	247.2
4	98.4	240.9	PD (34.6)	90.1	118.1 <sup>a)</sup>	4.55	70.1
5	100.8	244.1	PD (33.7)	81.9	100.0 <sup>a)</sup>	4.93	59.0
6C	141.7	266.1	PD (31.5)	45.7*	(55.5) <sup>b)</sup>	0.84	74.0
7	94.4	143.3	PD (32.3)	83.9	106.7 <sup>a)</sup>	5.07	55.9
8	101.6	149.6	PD (29.1)	81.9	120.1 <sup>a)</sup>	5.41	54.3
9C	138.6	204.7	PD (28.3)	52.0	(89.0) <sup>b)</sup>	1.09	55.1
10	105.5	156.7	46.4	83.1	119.7 <sup>a)</sup>	4.32	41.7
11	94.5	129.1	44.1	69.3	96.9 <sup>a)</sup>	4.03	48.8
12C	122.8	179.5	49.6 PPD	25.2*	(21.2) <sup>b)</sup>	0.33	56.7

PD: paper delamination  
 PPD: partial paper delamination  
 \*: one sample torn during measurement  
 a): some adhesive residue on sample edges  
 b): both samples torn

1. A removabl pressure-sensitiv adhesive tape comprising a highly extensible backing having a lengthwise elongation at break of at least about 150%, bearing on at least one major surface thereof a layer of photopolymerized acrylic pressure-sensitive adhesive comprising an acrylic polymer of monomers containing:

- a. at least about 70 parts of an alkyl acrylate monomer, the alkyl groups of which have an average of 4 to 12 carbon atoms, and,
- b. from 0 to about 30 parts of a monoethylenically unsaturated monomer, and
- c. from about 0.01 part to about 1 part of a photoinitiator,

said tape being capable of being firmly bonded to a substrate and being further capable of being removed therefrom after only being stretched at an angle no greater than about 35° from the surface of the substrate, wherein said adhesive tape is removable from a substrate substantially without leaving discernible adhesive residue on the substrate.

2. The removable pressure-sensitive adhesive tape of claim 1 wherein said alkyl acrylate monomer is selected from the group consisting of isooctyl acrylate, and butyl acrylate.

3. The removable pressure-sensitive adhesive tape of claim 2 wherein the monoethylenically unsaturated monomer is selected from moderately polar and strongly polar monomers.

4. The removable pressure-sensitive adhesive tape of claim 3 wherein the acrylic pressure-sensitive adhesive comprises an acrylic polymer of monomers containing:

- a) from about 75 to about 98 parts of isooctyl acrylate,

21

- b) from about 2 to about 25 parts of a monoethylenically unsaturated monomer selected from the group consisting of acrylic acid, and N-vinyl pyrrolidone.

5

5. The removable tape of claim 1 further comprising a crosslinking agent.

10

6. The removable tape of claim 1 further comprising from about 2 to about 20 parts of a hydrophobic silica.

15

7. The removable tape of claim 1 further comprising microspheres selected from nontacky polymeric microspheres and glass microspheres.

20

8. The removable tape of claim 7 wherein said backing is selected from the group consisting of polyolefins, vinyl copolymers, olefinic copolymers, acrylic polymers and copolymers, and combinations thereof.

9. The removable tape of claim 1 wherein said backing is colored.

25

10. A removable pressure-sensitive adhesive tape comprising a highly extensible backing having a lengthwise elongation at break of at least about 150%, bearing on at least one major surface thereof a layer of photopolymerized acrylic pressure-sensitive adhesive, said tape being capable of being firmly bonded to a substrate and being further capable of being removed therefrom after only being stretched at an angle no greater than about 35° from the surface of the substrate, wherein said adhesive tape is removable from a substrate substantially without leaving discernible adhesive residue on the substrate.

35

# INTERNATIONAL SEARCH REPORT

International Application No PCT/US 91/07779

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (if several classification symbols apply, indicate all) <sup>6</sup> According to International Patent Classification (IPC) or to both National Classification and IPC <b>IPC5: C 09 J 7/02, 133/08</b>						
<b>II. FIELDS SEARCHED</b> <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">Minimum Documentation Searched<sup>7</sup></div> <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 20%; border-bottom: 1px solid black;">Classification System</td> <td style="border-bottom: 1px solid black;">Classification Symbols</td> </tr> <tr> <td style="height: 40px; vertical-align: bottom;">IPC5</td> <td style="height: 40px; vertical-align: bottom;">C 09 J</td> </tr> </table> <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in Fields Searched<sup>8</sup></div>			Classification System	Classification Symbols	IPC5	C 09 J
Classification System	Classification Symbols					
IPC5	C 09 J					
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup></b>						
Category *	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>				
A	US, A, 3922464 (SILVER ET AL) 25 November 1975, see the whole document  --	1-10				
A	US, A, 4181752 (MARTENS ET AL) 1 January 1980, see the whole document  --	1-10				
A	US, A, 4223067 (LEVENS) 16 September 1980, see the whole document  --	1-10				
A	US, A, 4968562 (DELGADO) 6 November 1990, see the whole document  -----	1-10				
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p><b>* Special categories of cited documents:<sup>10</sup></b></p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&amp;" document member of the same patent family</p> </div> </div>						
<b>IV. CERTIFICATION</b>						
Date of the Actual Completion of the International Search  <b>5th February 1992</b>	Date of Mailing of this International Search Report  <b>7.4 FEB 1992</b>					
International Searching Authority  <b>EUROPEAN PATENT OFFICE</b>	Signature of Authorized Officer   <b>MISS T. TAZELAAR</b>					



**ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO.PCT/US 91/07779**

SA 53116

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.  
The members are as contained in the European Patent Office EDP file on 31/10/91  
The European Patent office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A- 3922464	25/11/75	AU-B- 445976 AU-D- 5606973 BE-A- 800064 CA-A- 988789 DE-A-B-C 2327452 FR-A-B- 2189489 GB-A- 1430136	07/03/74 07/03/74 26/11/73 11/05/76 06/12/73 25/01/74 31/03/76
US-A- 4181752	01/01/80	NONE	
US-A- 4223067	16/09/80	NONE	
US-A- 4968562	06/11/90	AU-D- 6928391 EP-A- 0444354 US-A- 4988567	29/08/91 04/09/91 29/01/91

For more details about this annex : see Official Journal of the European patent Office, No. 12/82